

LETTER TO THE EDITOR

Coupling of electronically excited physisorbed atoms to metal substrates: Xe on Au and Ti

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Abstract. From optical data in the energy range 5–11 eV it is deduced that the excited states of Xe physisorbed on clean Au and Ti surfaces couple strongly to conduction states in the metal substrate.

In this note we report an attempt to observe the optical excitation spectra of Xe atoms physisorbed on metal surfaces. Using apparatus capable of detecting coverages of a few hundredths of one monolayer on insulating surfaces, we have been unable to detect Xe coverages of a entire monolayer on clean Au and Ti surfaces. We interpret these results as evidence that the Xe excited state couples strongly to conduction electrons in the metal substrate and is broadened beyond our detection sensitivity by electron-hole pair creation in the metal.

The experiments employed photon reflection near grazing incidence (7°) for impurity atoms physisorbed at 10 K on metal films freshly prepared by evaporation. Photon counting and modulation techniques have been employed to give sensitivities of a few hundredths of a rare gas monolayer through the range 5–11 eV. The photon source was a hydrogen discharge lamp. Rare gas adsorbates were deposited onto clean films from crystal-calibrated sources that allowed precise coverages to be prepared as desired. The base pressure in the belljar was held below 10^{-9} Torr; in the He chamber containing the samples the pressure was probably below 10^{-11} Torr.

Typical signals from Xe adsorbed on a ceramic surface, in this case imperfectly cleaned glass, are provided for the purpose of illustration in figure 1. These data show that detailed spectra for physisorbed submonolayer films are readily accessible and available at very considerable signal to noise ratios. The data were obtained with plane polarised light. Multipliers given in figure 1 specify the scale factors for the individual runs. We observe Xe peak amplitudes that are in satisfactory proportion to coverages. Some spectral shifts occur as the coverage changes. Note that the residue of the $J = \frac{3}{2}$, $n = 2$ Xe excitation (arrow in figure 1) disappears as the coverage falls towards one monolayer. This is to be expected from its large orbital radius.

Figures 2 and 3 show the results for experiments conducted under identical conditions with Xe physisorbed on clean Au and Ti surfaces. The numbers on the curves give the density of Xe coverage in monolayers. The important point is that the

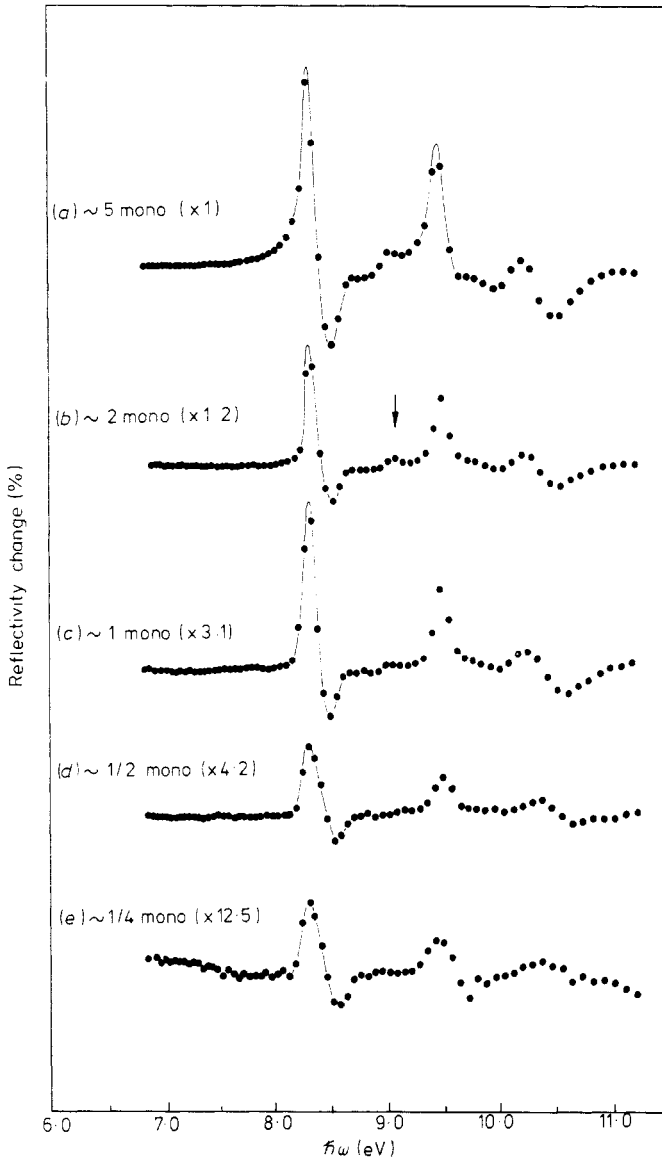


Figure 1. Reflection spectra of Xe on glass for various coverages. The coverages are given in monolayers, together with scale factors specifying the amplification.

absorption amplitude for m -monolayer films is approximately proportional to $m - 1$. No modified signal from the first monolayer can be clearly detected for films one monolayer or less in thickness, although slight residues of the spectra of thicker films can be traced in the spectra for low coverages. Clearly, the oscillator strength of the first layer has escaped detection.

Existing measurements for Xe dispersed in the alkali metals (Phelps *et al* 1976) and UPS results for Xe physisorbed on W (Waclawski and Herbst 1975) eliminate the possibility that the Xe oscillator strength is shifted completely out of our experimental energy range. Observed shifts are in fact small (≤ 1 eV). The spectra from

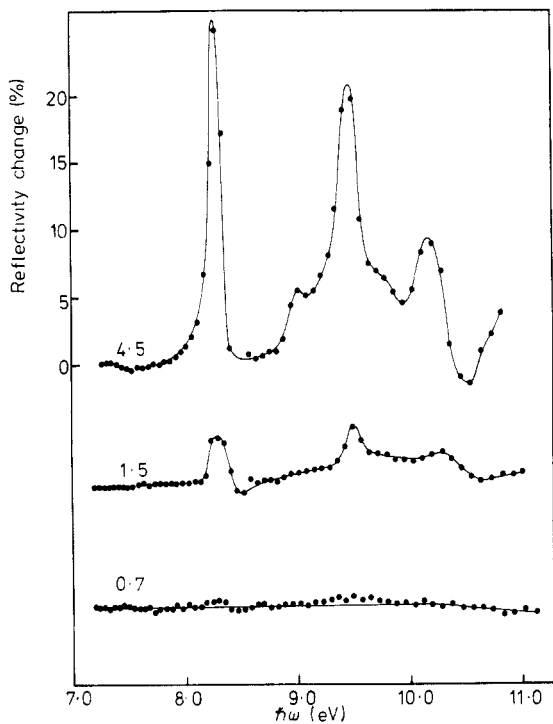


Figure 2. Reflection spectra for Xe on clean evaporated Au, with coverage specified in monolayers.

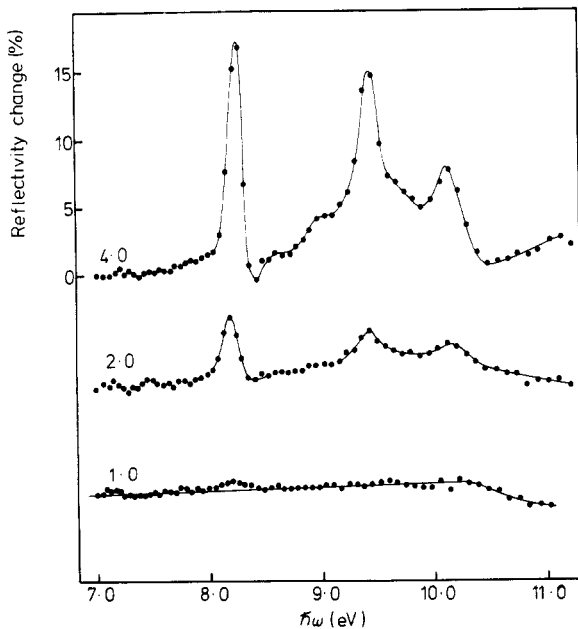


Figure 3. Reflection spectra for Xe on clean evaporated Ti, with coverage specified in monolayers.

insulator surfaces in figure 1 eliminate the possibility that the samples were improperly prepared owing to some overlooked experimental problem for low coverages. We therefore conclude that the Xe spectra are present but unobservable in the energy range of our experiments. We deduce that the Xe spectral lines from the metal surface must be an order of magnitude or more broader than those from Xe on the insulator surface.

It is most unlikely that a broadening of this magnitude could arise from lifetime limitations on the excited state. Even in bulk metals the Xe natural linewidth appears to be ≤ 0.1 eV (Phelps *et al* 1976). Phonon broadening of this magnitude seems quite out of the question. We therefore conclude that the Xe lines are broadened by interaction with the electron gas of the metal. The extra energy absorption must be the result of electron-hole pair excitation in the conduction band. Broadening of this type can be induced by the shock of the suddenly changed Xe self-consistent state.

Core lineshapes observed by photoemission often exhibit an asymmetric lineshape when the excitation is coupled to a metallic conduction band. The high-energy tail that causes this asymmetry arises from energy absorbed in band excitations. Evidence that the spectra of chemisorbed atoms are modified in this way is discussed by Gumhalter (1977). An observable asymmetry is not, however, a definitive test for coupling to conduction states since the core spectra of some good metals, notably the noble metals (see e.g. Hüfner and Wertheim 1975) lack marked high-energy tails. The absence of strong asymmetry from the 5p photoemission spectra of Xe physisorbed on W (Waclawski and Herbst 1975) therefore leaves the question of coupling to the band unresolved.

The effect of conduction electrons on photon spectra is more pronounced, and the present results lead us to conclude that the excitation is indeed strongly coupled to the conduction states. For host core spectra the coupling spreads optical lines into absorption shoulders, with continuum absorption above threshold. For the available Xe 5p oscillator strength, we deduce from our results that the lines from adsorbed Xe must be spread over 1 eV or more to escape detection. Lines of width equal to the Xe on W $P_{1/2}$ photoemission width (~ 0.5 eV of which ~ 0.25 eV is instrumental) could have been detected with ease. We conclude that the optical results provide strong evidence for the conduction electron broadening mechanism. The optical 5p-6s spectrum of Xe in alkali metals is spread over several eV, so the present lower bound of ~ 1 eV for Xe on Au and Ti appears reasonable provided that adsorbates and bulk impurities possess comparable couplings to band states.

It seems quite reasonable that surface excitations should cause electron-hole pair production comparable with that caused by local excitations in the bulk metal. Flynn (1976) has adapted the MND theory for internal excitation (see e.g. Nozières and de Dominicis 1969) to a model of surface excitations, to show that the two processes exhibit entirely analogous dependences on the electronic screening of the excited state. This similarity holds whether or not the MND extension to edge anomalies of Friedel's (1952) original model is applicable in detail to real materials. It is necessary only that the ground and excited configurations differ in their coupling to the conduction electrons. In the case of physisorbed Xe, the groundstate coupling may be neglected. However, it is easily established that the excited state coupling is always strong, so that our experimental observation of substantial band excitation is consistent with the present understanding of adsorbate structure. The way this excited state coupling arises is explained in what follows.

The valence chemistry of an excited Xe atom is very similar to that of Cs. This

similarity is documented by Phelps *et al* (1976); it arises from the weakness of the core differences between Xe* 5p⁵6s and Cs 5p⁶6s. An excited Xe atom on a Cs surface therefore resembles an adatom, with the electron gas extending through the Xe cell. Clearly, the coupling change is very large. Waclawski and Herbst (1975) and Antoniewicz (1977) assume that the Xe final state in photoemission is a positive ion owing to the ejection of a 5p electron. This cannot be true in general, but may be a satisfactory first approximation for the case of Xe on W. In the excited self-consistent state of Xe on Cs, for example, band states project entirely into the excited cell (which resembles an extra Cs cell) and the final states for photoemission and optical excitation possess little polar character (apart from band excitations, the optical and photoemission final states are locally identical when the excited centre is coupled to the conduction band and its lifetime exceeds the plasmon period). It is well known, however, that Cs on transition metal surfaces *does* transfer some charge to the substrate, so that in these cases the *ionic* state of Xe* may be an adequate approximation to the true adsorbate structure. Whether ionic or not, the core hole near the metal surface *must* be screened by an accumulation of one negative charge somewhere in its own vicinity. This charge shift, together with the strong Xe* (or Cs) 6s overlap with the metal surface, ensures that the excited configuration of Xe couples strongly to the metal substrate. The consequent coupling change accompanying excitation cause band excitations and associated line broadening. These are the effects we have deduced from the present experimental results.

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